Hydrogen–hydrogen interaction in an electron gas

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Abstract. We describe approximate methods for calculating the binding energy of two protons in an electron gas. For short interatomic separations, molecular-type binding is dominant; the model requires only one-centre spherical calculations for adding the density effect to the binding energy of the molecule in vacuum. For large separations, the pair potentials are obtained using a superposition of atom-in-jellium densities in a density functional including a new form of the kinetic energy which has several exact asymptotic behaviours. The binding energy curves are presented, for interatomic distances covering both the molecular and the asymptotic regions and for electron densities in the range $2.00 \leqslant r_s \leqslant 6.00$.

1. Introduction

Hydrogen in its condensed phases is very different from simple metals. Its particularities are due to the non-existence of deep core electrons screening the nucleus potential so that the conduction electron is not submitted to any orthogonalization constraint. As a result, the electron–ion interaction is strong in the range of normal metal densities and can never be treated using linear response (LR). This is reflected by the fact that the molecular structure of solid H survives under high pressures (2 or 3 Mbar) and that the proton potential can bind a level in an electron gas with a density parameter as low as $r_s = 2.00$ [1].

Much attention has been paid to the study of the electronic structure of H in an electron gas, and its changes with density [2–5]. This interest was motivated by the need to understand the experimental properties of metal hydrides [6,7], H solution in metals [8] and thermodynamic properties of hydrogen plasmas [9]. Although the simple model of H in jellium is a rather primitive picture of real systems, it has proven to be an excellent starting point for these studies. Naturally, the attempt to interpret the H–H interaction in various hosts has prompted the study of the binding properties of the H_2 molecule in an electron gas. This has been done first by Norskov [10] for short interatomic distances ($R \leqslant 2$ au). The approach used by this worker was to deal with the difference between the Green function of the electron gas containing H impurities and that of the unperturbed host. This difference, being localized in space, was then calculated self-consistently by expanding the solution of the Dyson equation on a localized basis set. Useful information was obtained about the one-electron spectrum, such as the change with density in the bonding and antibonding state energies in the range $r_s = 2.00$–4.00, and binding energy ϕ of the molecule as a function of the internuclear distance R. Obviously the long-range Friedel oscillations cannot be accounted for in this model so that the long-range behaviour of ϕ ($R > 2.0$ au) was not studied.

In the present work, we address the same problem of the pair interaction of two protons in an electron gas, using a completely different approach. We apply two distinct methods. One is for the short distances where the H_2 molecular structure is dominant, which requires

only one-centre calculations for adding the density effect to the binding energy of the molecule in vacuum. These calculations can be easily carried out with a standard program treating a spherical atom in jellium. The other method is specially aimed at treating large internuclear separations, in the spirit of the calculation of ion–ion interaction in simple metals. It is based on the use of a new formulation of the kinetic energy functional $T[n]$.

In section 2, we describe the model for the short distances R. The results are in good agreement with those of previously published work. Section 3 is devoted to the derivation of the kinetic energy functional and to its test for atomic H in jellium. The complete results for ϕ in the whole range of internuclear distances are discussed in section 4, and a conclusion is given in section 5 where possible extensions of this work are evoked.

2. Molecular binding at short internuclear distances

In the regime of normal metallic densities ($2.00 \leqslant r_s \leqslant 6.00$), the structure of a H_2 molecule in jellium shows important similarities to that of the free molecule [10]. The latter is in a bonding paramagnetic ground state for separations R up to 3 au, and a spin-polarized state is expected to appear for larger R [11]. As the paramagnetic state is favoured by an increase in electron density, it is likely that spin polarization does not occur for the molecule in jellium at distances $R < 3$ au. In the present section, we restrict our work to this range of internuclear separations.

The 'exact' calculation of the self-consistent electronic structure of a molecule in jellium, parallelling that commonly done using density-functional theory (DFT) for atomic impurities, is a very difficult numerical problem that has never been solved. Approximate methods are thus called for. A simple case is that of two weak scatterers, such as two alkali atoms; pseudopotentials and LR theory can be used in this case to determine ϕ with a quantitative accuracy, for internuclear distances larger than twice the core radius. The solution for shorter distances remains out of reach but has little practical interest for liquid simple metals. The case of H_2 is much more interesting with respect to technological applications. An approach to this problem has been developed in the framework of the effective-medium theory (EMT) [12], which expresses the total embedding energy of the molecule in a jellium of density n_0 as

$$E_m(R, n_0) = 2E_a(n_0 + \Delta n(R)) + \delta(R). \tag{1}$$

$E_a(n)$ is the embedding energy of a single H atom in a jellium of uniform density n. In equation (1), it is calculated with an effective jellium density $n_0 + \Delta n(R)$, $\Delta n(R)$ being the electron charge density displaced around the proton in a jellium of density n_0, at a distance R equal to the internuclear distance. $\delta(R)$ is a correction that we shall not explain here in detail. With this correction included, the energy in equation (1) agrees quite well [12] with the results of first-principles calculations solving for the localized part of the one-particle Green function [10].

In the following section we describe a different approximate model for calculating the H_2 binding energy.

2.1. The model

We establish an expression for the binding energy defined as

$$\phi(R, n_0) = E_m(R, n_0) - E_m(\infty, 0)$$

where $E_m(\infty, 0)$ is twice the energy of the H atom in vacuum. We start with the free-molecule binding energy $\phi(R, 0)$ and then take into account the change in density *at fixed R*. We write

$$\phi(R, n_0) = \phi(R, 0) + E_m^*(R, n_0) - E_m^*(R, 0) \tag{2}$$

assuming that this density change is well approximated, *for a fixed R*, by the density change in a pseudo-molecule energy E_m^*. This pseudo-molecule is an impurity in jellium for which only the part of the external potential having a spherical symmetry around the midpoint of the bond is retained:

$$V_m^*(r) = -2/\tfrac{1}{2}R \qquad \text{if } r < \tfrac{1}{2}R \tag{3a}$$

$$V_m^*(r) = -2/r \qquad \text{if } r \geqslant \tfrac{1}{2}R. \tag{3b}$$

E_m^* is readily calculated with a standard program for spherical impurities in jellium [13]. This approximation is expected to treat correctly the displaced density for $r \geqslant \tfrac{1}{2}R$ and to give a fair account of the Friedel oscillations at large r, but it does not estimate accurately the charge pile-up close to the nuclei, and we want to correct for this shortcoming. This is done by adding a correction $C_m(R, n_0)$ to $E_m^*(R, n_0)$. Having in mind the simple picture of the molecule as a superposition of two atoms, we write

$$C_m(R, n_0) = 2C_a(R, n_0) \tag{4a}$$

$$C_a(R, n_0) = E_a^*(0, n_0) - E_a^*(R, n_0) \tag{4b}$$

where $E_a^*(R, n_0)$ is the energy of a fictitious H atom in the external potential

$$V_a^*(r) = -1/\tfrac{1}{2}R \qquad \text{if } r < \tfrac{1}{2}R \tag{5a}$$

$$V_a^*(r) = -1/r \qquad \text{if } r > \tfrac{1}{2}R. \tag{5b}$$

$E_a^*(0, n_0)$ is clearly the exact energy $E_a(n_0)$ of a H atom in jellium, so that $C_m(R, n_0)$ is twice the difference between the exact energy of the atom and that of a pseudo-atom with its nucleus shifted from the centre of coordinates (both in jellium). Finally we obtain for ϕ

$$\phi(R, n_0) = \phi(R, 0) + E_m^*(R, n_0) - E_m^*(R, 0) + C_m(R, n_0) - C_m(R, 0) \tag{6}$$

with $C_m(R, n_0)$ defined by equation (4). Once again, all the quantities in equation (6) are calculable with a standard program in spherical symmetry. In order to have the exact limit at $R \to \infty$, $E_a^*(0, n_0)$ should be the energy of the ground-state atom in jellium. This atom has a doubly occupied bound state and its screening charge in the scattering states integrates to -1, but we do not expect this model to be able to describe the large separations, so that we can adopt a definition of E_a^* more adapted to small separations. It appeared more relevant to define E_a^* for small R as the energy of an excited pseudo-atom with single occupancy of the bound level and a free charge integrating to zero. This excited configuration is better for approximating the molecular density as a superposition; each atom contributes one bound electron to the doubly occupied bonding level of the molecule, and the superposed scattering states density still integrates to zero as it has to. In fact, calculations show that the functions $C_a(R, n_0)$ corresponding to these two atomic configurations ($1s^2$ or $1s$) remain proportional to an excellent accuracy when R increases. Their ratio is equal to the ratio of the displaced electron densities $\Delta n(r = 0)$ at the centre of coordinates, calculated in the two configurations with the nucleus at the centre of coordinates. For instance, at $r_s = 3.93$, $\Delta n(r = 0) = 0.354$ for $1s^2$ and 0.296 for $1s$. Thus, the magnitude of the correction is smaller for the excited configuration. This method for correcting equation (2) clearly requires that the atom in jellium carries a bound state; its range of validity is thus limited to $r_s < 2$ approximately.

2.2. Results

Numerical calculations have been performed according to equation (6) for internuclear distances R between 1 and 3 au. Five values of the density parameter have been selected: $r_s = 3.93$, 2.65 and 2.07 correspond to the electron densities for Na, Mg and Al, respectively, $r_s = 2.95$ has been added for comparison with other published theoretical results [14], and the value $r_s = 6.00$ is included in order to test the regime of very low densities. In table 1 we give the values of the embedding energy $E_m^*(R, n_0)$ of the spherical pseudo-molecule; the nucleus–nucleus interaction energy $1/R$ is not included since it plays no role in equation (6) once $\phi(R, 0)$ is known. In table 2 are reported the values of the correction $C_a(R, n_0)$. The values of the H_2 binding energy in vacuum are from the book of Hirschfelder *et al* [15]. The binding energy curves $\phi(R, n_0)$ are displayed in figure 1. Comparison with the results of Norskov [12] for $\phi(R_0, n_0)$, with $R_0 = 1.4$ au, is made in figure 2. Fair agreement is found between the two series of results obtained by completely different methods, although a slight deviation seems to appear at the highest densities. This gives confidence in the method proposed here.

Table 1. Embedding energy $E_m^*(R, n_0)$ of the spherical pseudo-molecule.

	$-E_m^*(R, n_0)$ (Ryd) for the following r_s					
R	∞	6.00	3.93	2.95	2.65	2.07
1.0083	4.0213	3.9903	3.9110	3.7758	3.6876	3.3583
1.2818	3.6557	3.6237	3.5433	3.4061	3.3164	2.9805
1.5042	3.4030	3.3707	3.2904	3.1529	3.0626	2.7229
1.7652	3.1478	3.1159	3.0368	2.8998	2.8093	2.4662
2.0714	2.8940	2.8635	2.7871	2.6515	2.5611	2.2147
2.4310	2.6451	2.6175	2.5452	2.4116	2.3214	1.9714
3.0904	2.2877	2.2681	2.2048	2.0746	1.9843	1.6267

Table 2. Correction $C_a(R, n_0)$, as defined in equation (4b).

	$-C_a(R, n_0)$ (Ryd) for the following r_s					
R	∞	6.00	3.93	2.95	2.65	2.07
1.0083	0.1200	0.1235	0.1322	0.1489	0.1586	0.1943
1.2818	0.1593	0.1639	0.1752	0.1976	0.2100	0.2552
1.5042	0.1893	0.1945	0.2079	0.2345	0.2497	0.3009
1.7652	0.2221	0.2278	0.2434	0.2747	0.2925	0.3497
2.0714	0.2571	0.2632	0.2811	0.3175	0.3360	0.4005
2.4310	0.2940	0.3000	0.3204	0.3605	0.3800	0.4518
3.0904	0.3514	0.3566	0.3813	0.4259	0.4479	0.5274

3. Ion–ion interaction at large internuclear distances

When two H atoms located at R_a and R_b in jellium are far apart, the superposition of two densities

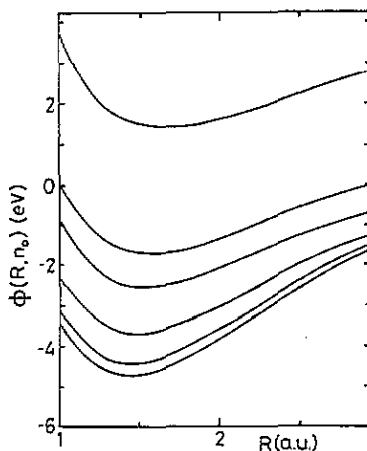$$\Delta n_m(r) = \Delta n(|r - R_a|) + \Delta n(|r - R_b|) \tag{7}$$

Figure 1. Binding energy of a H_2 molecule in an electron gas, as a function of internuclear distance for the regime of small separations. The lowest curve is for the molecule in vacuum. The other curves, with increasing minimum, correspond to $r_s = 6.00, 3.93, 2.95, 2.65$ and 2.07, respectively.
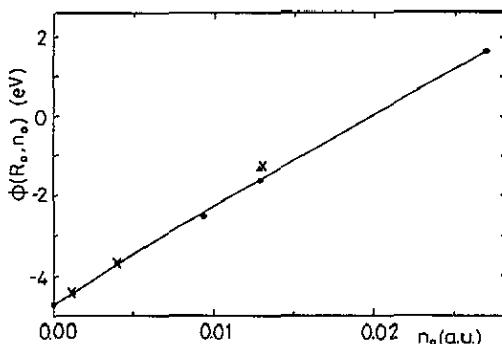

Figure 2. Binding energy of a H_2 molecule in an electron gas, at internuclear distance $R_0 = 1.4$ au, as a function of electron gas density: ●, this work; ×, from [12]; ▲, from [14].

with $\Delta n(r)$ the charge density displaced by a single H atom in jellium is expected to be a good approximation for the molecule. The underlying assumption is that the H–H interaction is not strong enough to perturb significantly the electronic structure in the vicinity of each nucleus. There are two criteria that can be used to determine the range of validity of such an approximation. One is that the bound state of the spherical pseudo-molecule defined in the previous section is not deeper than the bound state of the single atom, so that there is no additional binding due to overlap. The second criterion is that the density displaced by an atom at the site of the other is small compared with the average density n_0. We have always checked that both conditions are met when the model for large R given below is applied.

With the superposition of individual densities, we calculate the molecular energy as

$$\phi(R, n_0) = E[n_0 + \Delta n_a + \Delta n_b] - E[n_0 + \Delta n_a] - E[n_0 + \Delta n_b] + 1/R \qquad (8)$$

where $E[n]$ is the total energy functional for the molecule and Δn_a a short-hand notation for $\Delta n(|r - R_a|)$, the individual charge density at site a. Equation (8) is useful practically if one disposes of an explicit expression for $E[n]$. The crucial part is the kinetic energy functional. In the following sections, we propose a new form for this functional.

3.1. A new kinetic energy functional

Since DFT [16, 17] has rigorously established that the total energy of an electronic system in an external field is a unique functional of the electron charge density, there has been a permanent search for approximate forms of the kinetic energy functional [18]. A physically clear procedure to deal with this problem, in the case of a single s–p band of states, is to start with the exact expression of the kinetic energy in LR which is quadratic in Δn and to try to improve by adding higher-order effects. The LR form is

$$T_{LR}[n] = T_{TF}(n_0) + \mu_0 \Delta n(q = 0) - \tfrac{1}{2}(2\pi)^{-3} \int \Delta n(q) \frac{1}{\Pi_{LR}(q)} \Delta n(q)\, dq \qquad (9a)$$

where $T_{TF}(n_0)$ is the kinetic energy of the uniform electron gas, identical with the Thomas–Fermi (TF) kinetic energy for n_0. $\Delta n(q)$ is the Fourier transform of the displaced density $\Delta n(r) = n(r) - n_0$, and

$$\Pi_{LR}(q) = -(k_F/\pi^2) f(x) \qquad (9b)$$

is the Lindhard response function, k_F the Fermi momentum and

$$f(x) = \tfrac{1}{2} + [(1 - x^2)/4x] \ln[|(1 + x)/(1 - x)|] \qquad (9c)$$

with $x = q/2k_F$. In equation (9a), μ_0 is the kinetic contribution to the chemical potential or Fermi energy $\tfrac{1}{2}k_F^2$. Equation (9) is valid for any strength of the density gradient, but for small deviations from the average density only. Thus it is not applicable to strong perturbations such as the proton potential.

The link between the above functional and well known approximations such as the TF or Von Weizäcker (VW) approximations was clearly established by Jones *et al* [18]. The low-q limit of equation (9a) reproduces the second-order expansion of the TF functional; it amounts to replacing $f(x)$ by $f(0)$ in equation (9b). On the contrary, the large-q limit of the integral term in equation (9a) corresponds to the second-order form of the VW functional, i.e. $f(x) = 1/3x^2$ in equation (9b). As the TF approximation is the exact limit of the exact $T[n]$ for small density gradients, and the VW approximation is the exact limit for an atomic shell of electrons with s-symmetry, attempts have been made to build functionals having these correct limits. The simplest is

$$T_{TFG}[n] = T_{TF}(n) + T_{VW}[n] \qquad (10a)$$

$$T_{TF}(n) = \int \tfrac{3}{10}(3\pi^2)^{2/3} n^{5/3}\, dr \qquad (10b)$$

$$T_{VW}[n] = \tfrac{1}{8} \int \frac{|\nabla n|^2}{n}\, dr. \qquad (10c)$$

The equation above is different in spirit from the gradient expansion of the kinetic energy, where the coefficient in front of the second term is divided by nine, and which deals

only with small gradients. A large number of approximations based on equation (10*a*) with a non-constant coefficient in front of the gradient in T_{VW} have been proposed in the literature [19]. They have in common two shortcomings: they do not reduce exactly to T_{LR}, equation (9*a*), in the LR regime and they do not produce Friedel oscillations in the density at large distances. To correct for this, we suggest the following form:

$$T_{TFH}[n] = T_{TFG}[n] - \tfrac{1}{2}(2\pi)^{-3} \int \Delta n(q) \left(\frac{1}{\Pi_{LR}(q)} - \frac{1}{\Pi_{TFG}(q)} \right) \Delta n(q) \, dq. \tag{11}$$

Equation (11) uses the non-linear approximate form $T_{TFG}[n]$ where the $q = 0$ and $q \to \infty$ limits are correct to all orders and treats the intermediate values of q to second order in density by replacing their contribution already included in the leading term by that of equation (9*a*); thus, T_{TFH} firstly is correct to all orders at $q = 0$ and at large q and secondly reduces to T_{LR} if the density deviation is small so that it contains the logarithmic singularity at $q = 2k_F$. The functional of equation (11) has been successfully applied to the calculation of the lattice parameter, bulk modulus, vacancy formation energy, phonon dispersion curve, etc, in metallic sodium, using *ab-initio* molecular dynamics [20].

It is useful to look at the $n_0 \to 0$ limit of T_{TFH}. Let us rewrite this functional in the form

$$T_{TFH}[n] = T_{TFG}[n] + \Delta T_H[n] \tag{12a}$$

$$\Delta T_H[n] = \tfrac{1}{2}(2\pi)^{-3} \frac{\pi^2}{k_F} \int \Delta n(q) g(x) \Delta n(q) \, dq \tag{12b}$$

$$g(x) = 1/f(x) - 1 - 3x^2. \tag{12c}$$

$g(x)$ is a function having finite limits at $x = 0$ ($g(0) = 0$) and at $x \to \infty$ ($g(\infty) = -\tfrac{8}{5}$). When the average density n_0 of the material goes to 0, the integral in equation (12*b*) has a finite limit ($\Delta n(q)$ itself has a finite limit and $g(x)$ may be replaced by $g(\infty)$), so that $\Delta T_H[n]$ diverges as k_F^{-1}. This behaviour is incorrect. In order to avoid the divergence and to reproduce the finite atomic limit, ΔT_H may be 'delinearized', i.e. replaced by a functional containing higher orders in density, but keeping the same lowest-order form and having a finite limit for $n_0 = 0$. The procedure is easier to carry out in *r*-space. We 'delinearize' $\Delta n(r)$ through the substitution

$$\Delta n(r) \to \alpha^{-1}(n_0)^{1-\alpha}\{[n_0 + \Delta n(r)]^\alpha - (n_0)^\alpha\}$$

and choose α in order to cancel the divergence at $n_0 = 0$. This gives $\alpha = \tfrac{5}{6}$. Thus, we have the approximation

$$T_{TFM}[n] = T_{TFG}[n] + \Delta T_M[n] \tag{13a}$$

$$\Delta T_M[n] = \tfrac{1}{2} K \int F(r) g(r - r') F(r') \, dr \, dr' \tag{13b}$$

with $K = \tfrac{1}{3}(3\pi^2)^{2/3}$ and

$$F(r) = \tfrac{6}{5}[n(r)^{5/6} - (n_0)^{5/6}]. \tag{13c}$$

The $n_0 = 0$ limit of ΔT_M is now $\Delta T_M = -\tfrac{32}{25} T_{TF}(n)$. But, at $n_0 = 0$, the exact limit for a single-level system is T_{VW}. So, we should obtain an exact cancellation between ΔT_N and

Table 3. Comparison of the kinetic energy contribution to the embedding energy of a H atom in jellium, in various approximations. All are computed with the electron charge density resulting from the self-consistent DFT calculation with the electron gas average density n_0 considered. Wigner exchange–correlation energy. T_{LR} is from equation (9a), T_{TFG} from equation (10a), T_{TFH} from equations (12), T_{TFM} from equations (13) and T_{TFN} from equations (14). T_{DFT} can be considered as 'exact'.

r_s	T_{LR} (Ryd)	T_{TFG} (Ryd)	T_{TFH} (Ryd)	T_{TFM} (Ryd)	T_{TFN} (Ryd)	T_{DFT} (Ryd)
6.00	36.347	1.7217	−0.8684	0.7542	0.9519	0.9639
3.93	11.743	1.7678	−0.0474	0.8572	1.0368	1.0509
2.95	6.3056	1.8695	0.4848	1.0250	1.1850	1.1987
2.65	5.1739	1.9388	0.6231	1.1221	1.2738	1.2880
2.07	3.7350	2.2077	1.1141	1.4557	1.5879	1.5975
1.50	3.4273	2.9297	2.0377	2.2508	2.3591	2.3703
1.30	3.7166	3.4626	2.6349	2.8099	2.9086	2.9126
1.00	4.9493	4.9772	4.2375	4.3619	4.4451	4.4252

T_{TF} at $n_0 = 0$. We can impose this cancellation by modifying once again the third and higher orders in ΔT_M. The solution is obviously not unique. A simple solution consists in multiplying $F(r)$ by

$$m(r) = (n_0 + \nu \Delta n)/(n_0 + \Delta n)$$

with $\nu = 5/\sqrt{32}$. Thus, our final kinetic energy functional is

$$T_{TFN}[n] = T_{TFG}[n] + \Delta T_N[n] \tag{14a}$$

$$\Delta T_N[n] = \tfrac{1}{2} K \int G(r) g(r - r') G(r') \, dr \, dr' \tag{14a}$$

$$G(r) = m(r) F(r). \tag{14c}$$

Let us recall the properties of this functional. T_{TFN} is exact to second order in $\Delta n(q)$ for any q. It coincides with the TF functional for very high densities with small gradients, and it is exact in the $n_0 = 0$ limit for a single-level system. Let us also mention that in this latter limit the VW functional is exact not only for the s-symmetry atom, but also for a two-centre single-level system; it is easy to check that the VW functional gives the 'exact' kinetic energy of the H_2 (or H_2^+) molecule with a determinantal singlet or triplet molecular wavefunction $\psi(r, r')$, the density $n(r)$ to be used in the functional being

$$n(r) = 2 \int \psi^*(r, r') \Psi(r, r') \, dr'$$

with ψ normalized to unity.

3.2. Results for H in jellium

We have performed 'exact' self-consistent DTF calculations for a proton in jellium, solving the Kohn–Sham equations. With the displaced electron charges obtained, we have calculated the kinetic energies using the five functionals T_{LR}, T_{TFG}, T_{TFH}, T_{TFM} and T_{TFN}. The results are shown in table 3 for values of r_s from 6.00 to 1.00. The approximations T_{LR}, T_{TFG} and T_{TFH} are rather poor at low densities; they become better at higher densities, as expected. T_{TFM} and T_{TFN}, which do not diverge at low density like T_{TFH}, are significantly better; the exact cancellation of the TF contribution for $n_0 = 0$ imposed on T_{TFN} produces a marked improvement.

Some comments are relevant before considering the Euler equations associated with these functionals. Firstly, at the densities considered, $r_s \geqslant 2.07$, there is a bound state in the spectrum of H in jellium. This bound state becomes deeper when the density decreases; its eigenvalue is -0.0181 Ryd at $r_s = 6.00$, and the average of r is $\langle r \rangle = 3.75$ for this bound state. Nevertheless, the good results obtained for the kinetic energy in the low-density regime prove that T_{TFN} is able to treat not only a single-band spectrum, but also a more complex spectrum with a shallow bound state. Secondly, although T_{TFN} is exact for the *molecule in vacuum*, we have found that it gives total energies which are too low for the *molecule in jellium* at $r_s = 6.00$ and equilibrium separation. The reason is that the bound state is much lower for the molecule in jellium than for the free atom, so that T_{TFN} is unable to represent this bound state and the continuum together. This means that, although exact at $n_0 = 0$, T_{TFN} does not have the correct density dependence at very low n_0. The dependence on low n_0 is related to the response function of the localized system and involves excited states in vacuum. It would be very difficult to include in a kinetic energy functional, but a possible further improvement could be to ensure that the total energy satisfies the exact relation

$$\frac{\mathrm{d}E_a(n_0)}{\mathrm{d}n_0} = - \int V_H(r) \, \mathrm{d}r$$

where V_H is the Coulomb potential of the system [21].

3.3. Euler equation

Good results for the total energy of *atomic* H in jellium may be obtained with functionals which would not generate correct displaced densities. Before using a given functional together with the 'exact' single-atom density for calculating the pair interaction with the help of equation (8), it is important to realize that the large cancellations which occur in such an expression will not be handled correctly if the Euler equation

$$\delta E[n]/\delta n(r) = \mu$$

is not satisfied with enough accuracy for the 'exact' charge density and the approximate $E[n]$. There are two ways to check that the Euler equation is approximately verified. The first is to check that the total energy is variational with respect to small deviations in the charge density around the DFT density. The second method is to calculate explicitly the functional derivative for the DFT density and to see how much it deviates from μ. We have tried both methods.

The stationary property has been studied by calculating the total energy of the H atom in jellium with T_{TFN} and a 'rescaled' density:

$$\Delta n_\lambda(r) = \Delta n_{DFT}(r) - (A/\pi) \exp(-2r) + (A/\pi)\lambda^{-3} \exp(-2\lambda r). \qquad (15)$$

This form has the advantage of preserving the correct asymptotic form of the electron charge that a simply rescaled $\Delta n_{DFT}(\lambda r)$ would not have. The rescaled density of equation (15) is normalized, and A is the largest possible value in the range 0–1 such that $n_0 + \Delta n_\lambda(r)$ is strictly positive everywhere. We show two examples in table 4. At $r_s = 6.00$, one obtains the total energy minimum for $\lambda = 1.006(A = 1)$, with a total energy $E_a = -1.09276$ Ryd (E_a is exactly equal to -1.08160) and a kinetic energy $T = 0.96207$ (T is exactly equal to 0.96393). At $r_s = 2.65$, the total energy at minimum is $E_a = -1.03323$ (E_a is exactly equal to -1.028800) and $T = 1.29981$ (T is exactly

equal to 1.288 00); this minimum is reached at $\lambda = 1.013$. We can conclude that the effect of rescaling is small, but non-negligible. It indicates that the Euler equation associated with T_{TFN} is not exactly satisfied by the exact DFT density. The functional T_{TFN} leads to total energies that are lower than the exact energies. Nevertheless, the improvement shown by T_{TFN} with respect to T_{TFG} is emphasized by the following values: the latter functional gives a minimum energy $E_a = -0.685\,35$ at $\lambda = 0.65$, with a kinetic energy $T = 0.924\,29$.

Table 4. Minimization of the total energy $E[n_0 + \Delta n] - E[n_0]$ of a H atom in jellium with the kinetic energy functional T_{TFN}, using a rescaled charge density. T is the kinetic energy. λ is the scaling parameter, equation (15).

$r_s = 6.00$			$r_s = 2.65$		
λ	E (Ryd)	T (Ryd)	λ	E (Ryd)	T (Ryd)
0.990	−1.092 50	0.935 20	0.990	−1.032 51	1.254 18
1.000	−1.092 72	0.951 63	1.000	−1.032 99	1.273 84
1.003	−1.092 75	0.956 99	1.005	−1.033 14	1.283 77
1.006	−1.092 76	0.962 07	1.010	−1.033 21	1.293 78
1.010	−1.092 75	0.968 87	1.013	−1.033 23	1.299 81
			1.015	−1.033 23	1.303 85
			1.020	−1.033 17	1.313 99

Now we consider directly the Euler equation associated with the functional T_{TFN}. It can be written, with $n = n_0 + \Delta n$

$$\frac{1}{2}K(n^{2/3} - n_0^{2/3}) + \frac{1}{8}\left(\frac{|\nabla n|}{n}\right)^2 - \frac{1}{4}\frac{\nabla^2 n}{n} + K\frac{\delta G(r)}{\delta n(r)}\int g(r - r')G(r')\,dr'$$

$$+ \int \frac{1}{|r - r'|}\Delta n(r')\,dr' + V_{xc}(n) - V_{xc}(n_0) = \frac{1}{r}. \tag{16}$$

We have calculated the Fourier transform $Q(q)$ of the left-hand side of equation (16) with the DFT density Δn_{DFT}, which should be equal to $v(q) = 4\pi/q^2$ if the functional were identical with the DFT functional. In figure 3, we display $Q(q)/v(q)$ at $r_s = 3.93$ and compare it with functionals including other kinetic forms. The larger the deviation of the ratio from unity, the poorer is the approximation of the kinetic functional. We see that T_{LR} is a very poor approximation. T_{TFG} is better but has an important maximum deviation at $x = 1.2$ and goes very slowly towards its asymptotic value at large q. This asymptotic limit equal to 1 reflects the fact that the kinetic functional treats the large gradients of the density exactly to all orders (this is not done by T_{LR} where these gradients are taken into account to second order only). The functional T_{TFN} is excellent for $x > 3$, but the vicinity of $x = 1$ is still suffering some imperfection. This is because T_{TFN} is not able to deal with the correct phase of the density. When the Euler equation is analysed in detail, one can see that the singularity at $x = 1$ comes from $\Pi_{LR}(q)$ only, exactly as in the LR case. The exact treatment of the singularity, involved in the asymptotic form of the DFT density, requires a functional exact to higher orders. Attempts to include a quasi-exact contribution of order three in density in the kinetic functional have been reported in the literature, but they lead to considerable practical difficulties [22, 23]. To conclude this section on kinetic energy functionals, let us say that the quality of T_{TFN}, measured by the deviation $Q(q)/v(q)$ from unity, improves when the average density increases, as expected.
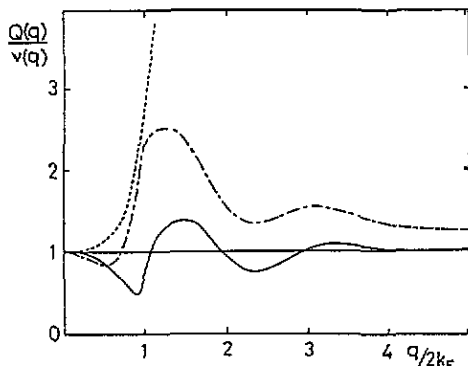
Figure 3. Test of how the DFT charge density solves the Euler equation associated with various kinetic energy functionals: ——, T_{FN}; — · —, T_{TFG}; – – –, T_{LR}. $Q(q)$ is the effective external *potential extracted from the Euler equation, in reciprocal space. It should be equal to the bare* Coulomb potential $v(q)$ if the functional were exact.
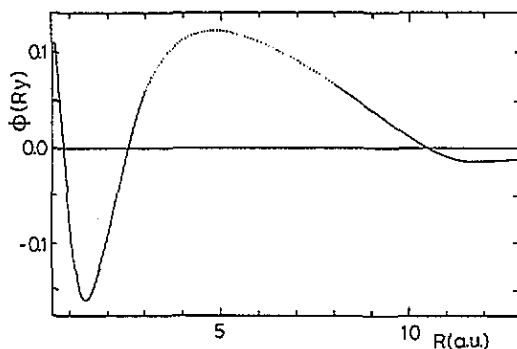

Figure 4. The H–H interaction in jellium with $r_s = 6.00$. For $R < 3$ au, the molecular binding model is used, and for $R \geqslant R_m = 8$ au the large-distances model (——): · · · · · ·, between 3 and 8 au, curve obtained by a numerical interpolation.

3.4. Pair interaction calculation

With the functional T_{TFN} defined in equation (14), we have calculated the pair interaction $\phi(R, n_0)$ given in equation (8), using for the single-site density the self-consistent DFT $\Delta n(r)$. The differences between the energy for the overlap of densities and the single site energies were calculated successively for the kinetic, Coulomb and exchange-correlation contributions. It was checked that rescaling the density, according to equation (15), did not allow the energy to decrease in the range of large internuclear distances treated with this model. The calculations were done, when possible, in r-space. For instance, an integral of the form

$$\int J[n_0 + \Delta n(r) + \Delta n(|r + R|)]\, dr$$

was transformed to

$$\frac{2\pi}{R} \int_0^\infty r\, dr \int_a^b x\, dx\, J[n_0 + \Delta n(r) + \Delta n(x)] \tag{17}$$

Table 5. $\phi(R, n_0)$ as defined in equation (8). R_m is the minimum internuclear distance for which the large-R model is applicable.

R (au)	$2k_F R$ (au)	ϕ (Ryd) $r_s = 6.00$	ϕ (Ryd) $r_s = 3.93$
1.000		−0.067 89	0.001 32
1.250		−0.146 62	−0.081 08
1.500		−0.162 00	−0.101 11
1.750		−0.136 50	−0.081 05
2.000		−0.100 70	−0.051 24
2.250		−0.055 29	−0.012 06
2.500		−0.009 65	0.027 30
2.750		0.027 44	0.058 17
3.000		0.058 27	0.082 16
	2.000	0.071 63	
	2.500	0.119 56	
	3.000	0.132 20	0.087 74
	3.500	0.127 18	0.106 63
	4.000	0.112 41	0.106 67
	4.500	0.093 38	0.090 87
	5.000	0.084 14	0.072 52
	5.500	0.054 69	0.051 10
	6.000	0.026 03	0.031 34
	6.500	0.005 96	0.014 15
	7.000	−0.007 36	0.000 59
	7.500	−0.013 11	−0.008 76
	8.000	−0.013 82	−0.011 38
	8.500	−0.011 35	−0.012 80
	9.000	−0.007 46	−0.009 99
	9.500	−0.003 21	−0.005 48
	10.00	0.000 36	−0.001 53
	10.50	0.002 84	0.002 09
	11.00	0.004 05	0.004 33
	11.50	0.004 08	0.004 98
	12.00	0.003 23	0.004 35
	12.50	0.001 91	0.002 96
	13.00	0.000 54	0.001 42
	13.50	−0.000 70	−0.000 34
	14.00	−0.001 50	−0.001 52
	14.50	−0.001 79	−0.002 17
	15.00	−0.001 64	−0.002 15
R_m (au)		8.00	5.80
$2k_F R_m$ (au)		5.12	5.66
$E[n_0 + \Delta n] - E[n_0]$ (Ryd)		−1.081 60	−1.085 22

with the help of a change in variable $x = |r + R|$. The integration limits are $a = |R - r|$ and $b = R + r$. We shall not explain further the details of these calculations, except for mentioning that for the term $\Delta T_N[n_0 + \Delta n(r) + \Delta n(|r + R|)]$, and for it only, we made an approximation for the function G (equation (14c)):

$$G(r) = G(n_0 + \Delta n(r) + \Delta n(|r + R|)) \simeq G(n_0 + \Delta n(r)) + G(n_0 + \Delta n(|r + R|)) - G(n_0).$$

(18)

Without such an approximation, the two-centre double integration involved in ΔT_N is very difficult to calculate. With equation (18), it is easily estimated in reciprocal space.

Table 6. $\phi(R, n_0)$ as defined in equation (8). R_m is the minimum internuclear distance for which the large-R model is applicable.

R (au)	$2k_F R$ (au)	(Ryd) $r_s = 2.95$	$r_s = 2.65$	$r_s = 2.07$
1.000		0.033 79	0.039 87	0.031 35
1.250		−0.057 16	−0.054 48	−0.073 72
1.500		−0.086 26	−0.089 07	−0.117 62
1.750		−0.075 67	−0.083 48	−0.120 15
2.000		−0.055 49	−0.064 61	−0.110 67
2.250		−0.023 43	−0.033 97	−0.088 03
2.500		0.009 68	−0.002 56	−0.063 12
2.750		0.036 32	0.021 29	−0.039 33
3.000		0.056 01	0.039 08	−0.017 07
	4.000	0.059 83		
	4.500	0.064 22	0.044 75	
	5.000	0.056 59	0.045 36	
	5.500	0.043 85	0.037 70	
	6.000	0.030 18	0.028 17	0.000 23
	6.500	0.017 63	0.017 93	0.011 36
	7.000	0.005 87	0.005 80	0.008 40
	7.500	−0.004 79	−0.004 19	−0.001 53
	8.000	−0.010 91	−0.010 06	−0.007 40
	8.500	−0.011 68	−0.011 81	−0.010 06
	9.000	−0.010 55	−0.010 44	−0.009 49
	9.500	−0.007 14	−0.007 28	−0.007 35
	10.00	−0.002 50	−0.003 12	−0.003 71
	10.50	0.000 92	0.000 50	−0.000 56
	11.00	0.003 28	0.003 27	0.002 18
	11.50	0.004 69	0.004 59	0.003 72
	12.00	0.004 39	0.004 57	0.004 09
	12.50	0.003 12	0.003 51	0.003 36
	13.00	0.001 81	0.001 93	0.002 13
	13.50	0.000 40	0.000 30	0.000 65
	14.00	−0.001 15	−0.001 18	−0.000 80
	14.50	−0.002 13	−0.002 08	−0.001 71
	15.00	−0.002 22	−0.002 32	−0.002 14
R_m (au)		4.60	4.20	3.70
$2k_F R_m$ (au)		5.99	6.08	6.86
$E[n_0 + \Delta n] - E[n_0]$ (Ryd)		−1.050 36	−1.019 04	−0.883 31

4. Complete Results

The pair interaction is given in tables 5 and 6 for the whole range of R-values. The origin of energies is as in equation (8), so that $\phi(R, n_0)$ goes to zero at infinite separations. This choice implies a shift in the values calculated in section 2 for $R \leqslant 3$, where the molecular binding energy was measured with respect to the energy of two isolated atoms in vacuum. As already mentioned, the model used for large distances is not applicable in the range $R \leqslant R_m$. R_m is also shown in tables 5 and 6. R_m is determined as the internuclear distance for which the bound level energy of the pseudo-molecule defined in section 2.1, equation (3), equals that of the H atom (very shallow) at the same n_0. We have seen in the atomic case that the kinetic functional T_{TFN} is able to treat the corresponding spectrum correctly, bound and free parts as a whole. With this R_m, the H displaced density is such that $\Delta n(r)/n_0$ is smaller than 0.12 at $r_s = 6.00$ and 0.22 at $r_s = 2.07$ for all $r > \frac{1}{2}R_m$.
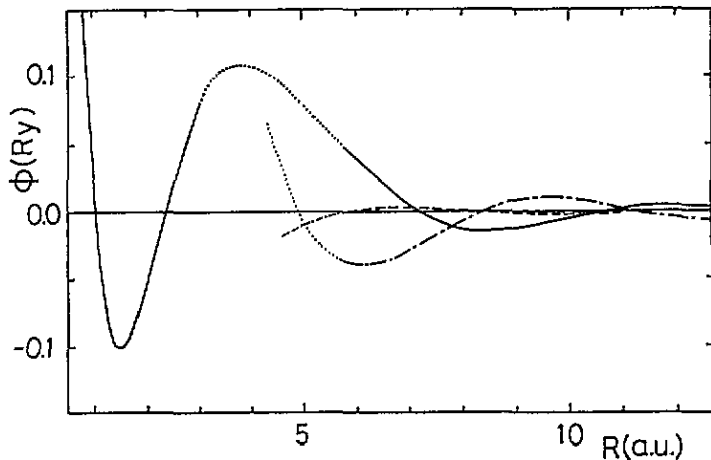
Figure 5. Same as figure 4, but for $r_s = 3.93$. Two other approximations for the large distances are also shown: $- - -$, ϕ_a, equation (19); $- \cdot -$, ϕ_b, equation (21).
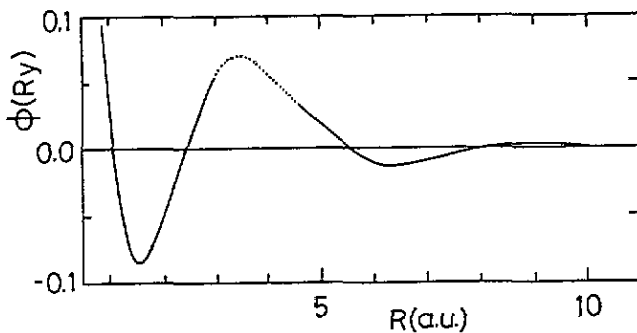

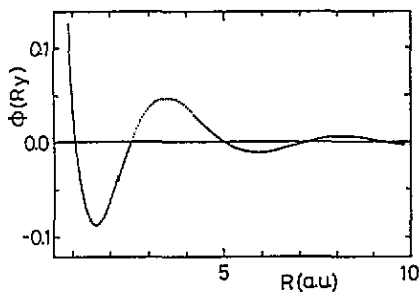Figure 6. Same as figure 4, but for $r_s = 2.95$.

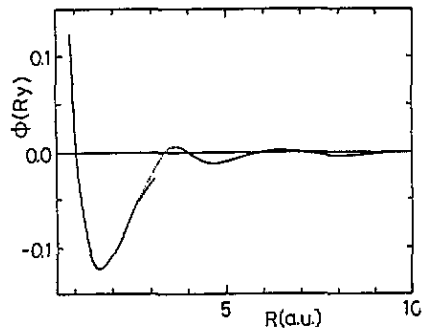Figure 7. Same as figure 4, but for $r_s = 2.65$.

Figure 8. Same as figure 4, but for $r_s = 2.07$.

For distances between 3 au and R_m, ϕ has been determined using numerical interpolation. As shown in figures 4–8, there is no difficulty in joining smoothly the results of the two models obtained separately in regions $R \leqslant 3$ and $R \geqslant R_m$. This is particularly

obvious at $r_s = 2.95$ and 2.65, where R_m is not very far from 3. At $r_s = 2.07$, the results given by the molecular model seem slightly too low for a perfect match with the curve resulting from the second model. This can be related to the fact shown in figure 2 where it appeared that our molecular binding energy was slightly underestimated with respect to the results of Norskov [12]. Thus, we think that $r_s = 2.07$ is the lowest electron density parameter which can be treated by our molecular binding model.

In order to demonstrate the effect of using an elaborate kinetic energy functional instead of more simple approximations, we have also displayed in figure 5 ($r_s = 3.93$) the pair interaction calculated as follows:

(a) using the full LR form of the pair interaction, i.e.

$$\phi_a(q) = v(q) + v(q)\chi(q)v(q) \tag{19}$$

where $\chi(q)$ is the density response function given by

$$\chi(q) = \Pi_{LR}(q)/\{1 - [v(q) + X]\Pi_{LR}(q)\} \tag{20}$$

including local field effects through $X = dV_{xc}(n_0)/dn_0$;

(b) with an approximation frequently used in the theory of simple metals, where a pseudopotential $w(q)$, which would give the DFT charge density in the LR, replaces the bare proton potential $v(q)$:

$$\phi_b(q) = v(q) + w(q)\chi(q)w(q) \tag{21}$$

$$w(q) = \Delta n_{DFT}(q)/\chi(q) \tag{22}$$

These two approximations ϕ_a and ϕ_b differs very markedly from the calculation with T_{TFN} and would be much more difficult to reconcile with the molecular model.

5. Conclusion

We have reported a study of H_2 binding in an electron gas, using two methods, each of them being well suited to one of the two regimes of internuclear separations. The first treats the region of molecular binding ($R \leqslant 3$ au) where the electronic structure is reminiscent of the free-molecule structure. The density dependence is accounted for by adding contributions which are readily calculated in spherical symmetry (i.e. with a standard numerical program) to the free-molecule binding energy. The results are in good agreement with those obtained in other work. The second method, which treats large internuclear distances, assumes that an overlap of the charge density displaced by a single atom in jellium is a good approximation for the molecule and makes use of a new kinetic energy functional described at length in this paper. The binding energy curves resulting from these two models in their respective domains match easily.

This work may have a number of extensions. First, the methods developed here can be straightforwardly applied to the case where the uniform background contains a cavity, which is believed to be more realistic for describing substitutional impurities. Second, the effect of temperature can be included without theoretical difficulty for application to H plasmas [24]. Also, the functional T_{TFN} might be of some use for people doing molecular dynamics calculations with a 'true' density functional [20]. Finally, this functional could provide a new approximation in the theory of simple liquid metals, especially in cases where non-linear effects are expected to play some role in pair interactions [25].

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